

Crystal property engineering using molecular–supramolecular equivalence: Mechanical property alteration in hydrogen bonded systems

Saikat Mondal,^a C. Malla Reddy,^{*a, b} Subhankar Saha^{*c}

^aDepartment of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, 741246, Nadia, West Bengal, India. E-mail: cmallareddy@gmail.com

^bDepartment of Chemistry, Indian Institute of Technology Hyderabad, Kandi 502284, Telangana, India. E-mail: cmallareddy@gmail.com

^cDepartment of Chemistry, Islampur College, Islampur, Uttar Dinajpur, West Bengal, 733202 India. E-mail: subho.chem09@gmail.com

Table of Contents

Sl. No.	Contents	Page No.
1.	Experimental details (S1-S6)	2-4
2.	Computational details (S7)	5
3.	Figures (S8-S16)	5-10
4.	Crystallographic information table (S17)	11
5	Comparison of crystallographic parameters between 3 and 4 (S18)	12
6	Supplementary Movies (S19)	12
5.	References	12

S1: Synthesis

Compound 4:

To synthesize compound **4** a previously reported procedure was followed with some modifications.¹ 4-Hydroxybenzyl alcohol (1.0 equiv) was dissolved in anhydrous THF (25 mL), under an atmosphere of N₂, followed by the addition of Et₃N (1.0 equiv). The reaction mixture was stirred for 5 min, after which the 4-nitrobenzoyl chloride (1.1 equiv) in 25 mL DCM solution was added dropwise. The resultant mixture was stirred and refluxed at 70 °C until the completion of the reaction indicated by TLC. The reaction was quenched by adding brine (30 mL), and the aqueous solution was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica column chromatography and characterized by ¹H NMR technique.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.35 (m, 4H), 7.38 (d, 2H), 7.25 (d, 2H), 5.23(t, 1H), 4.50 (d, 2H).

Compound 5:

The same synthetic procedure as of compound **4** was followed but using corresponding benzoyl chloride and 4-hydroxybenzyl alcohol derivatives.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.41 (m, 4H), 7.30 (s, 1H), 7.22 (m, 2H), 5.23(t, 1H), 4.50 (d, 2H), 2.17 (s, 3H).

4-(hydroxymethyl)phenyl 4-bromobenzoate:

The same synthetic procedure as of compound **4** was followed using corresponding benzoyl chloride and 4-hydroxybenzyl alcohol derivatives.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.05 (d, 2H), 7.82 (d, 2H), 7.40 (d, 2H), 7.23 (d, 2H), 5.26 (t, 1H), 4.52 (d, 2H).

Compound 7:

The same synthetic procedure as of compound **4** was followed using corresponding benzoyl chloride and 4-hydroxybenzyl alcohol derivatives.

S2: Crystallization method

To perform crystallization experiments, adequate amount of the synthesized compounds were separately dissolved in different organic solvents (see the below table) and left for slow evaporation crystallization. Visually good, diffraction quality single crystals were obtained from dichloromethane (DCM) solutions after 2-3 days.

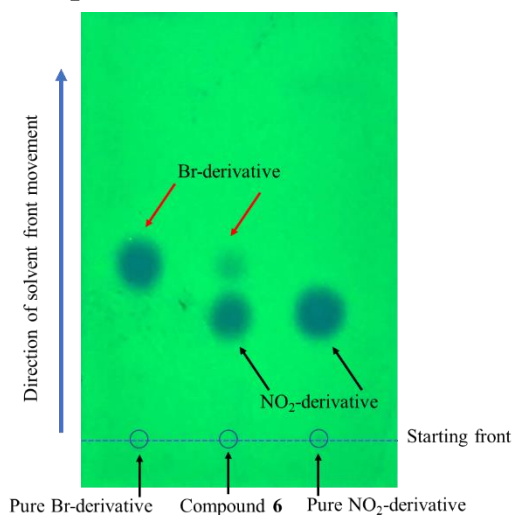
For crystallization of compound **6** (solid solution), equimolar amount of both compounds 4-(hydroxymethyl)phenyl 4-nitrobenzoate and 4-(hydroxymethyl)phenyl 4-bromobenzoate were dissolved in different solvents (see below table) and left for slow evaporation crystallization. Visually good, diffraction quality single crystals were obtained from dichloromethane (DCM) solutions after 2-3 days.

S2a: Different solvent conditions for crystallization

Solvent	Compound			
	4	5	6	7
DCM	✓	✓	✓	✓
THF	✓	✓	✓	✓
Ethyl acetate	✓	✓	-	✓
Acetonitrile	✓	✓	-	✓

✓ Crystals of the same form (as reported in the manuscript) were obtained.

S2b: TLC experiment for the solid-solution crystals, **6**



The presence of both nitro and bromo derivatives was noted in a TLC experiment using 3:7 ethyl acetate and hexane solvent mixture for a crystal of compound **6**.

S3: Single crystal X-ray diffraction (SCXRD)

X-ray diffraction data for the crystals were collected at ambient condition using a Rigaku (dual, Cu/Mo at zero, Eos) diffractometer with monochromatic CuK α ($\lambda = 1.54184 \text{ \AA}$) source having a 100 μm beam size. The structure was solved with the SHELXT 2014/4 solution program² using iterative methods and by using Olex2 1.5-dev³ as the graphical interface. The model was refined with olex2.refine 1.5-dev⁴ using full matrix least squares minimization on F^2 . The anisotropic displacement parameters of all non-hydrogen atoms were refined. Mercury (3.10.1 version) was used to create all of the crystal packing diagrams.

S4: Powder X-ray Diffraction (PXRD)

The PXRD patterns of compound **4** had been collected using a CuK α radiation (1.540 \AA) on a Rigaku SmartLab. The tube voltage and current were chosen as 40 kV and 50 mA, respectively. With a step size of 0.02 $^\circ$, each sample was scanned between 5 and 50 $^\circ$ 2θ . A silicon standard was used to calibrate the instrument before the experiment.

S5: Nanoindentation

Nanoindentation experiments were performed on the (011) face of single crystals of **4** at maximum load of 1 mN and 5 mN respectively using the TI Premier from Hysitron, Minneapolis, USA, equipped with an in-situ Scanning Probe Microscope (SPM). To determine the hardness (H) and elastic modulus (E) of the crystals a Berkovich tip (three-sided pyramidal tip with a total included plane-edge angle of 142.3 $^\circ$) of radius \sim 150 nm was used. The standard Oliver-Pharr method⁵ is used to extract the H and E . The same procedure was followed for nanoindentation experiments on the (011) face of crystals of **5**, **6** and (001) major face of crystals of **7** at maximum load of 5 mN.

S6: Differential scanning calorimetry (DSC)

DSC experiments were performed on a PerkinElmer DSC 400 instrument on accurately weighed samples (1.5 mg of compound **4**) placed in hermetically sealed aluminium crucibles (40 μL) upon scanning in the range of 25 $^\circ\text{C}$ to 275 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C}/\text{min}$ under a dry nitrogen atmosphere (flow rate 80 mL/min).

S7: Energy frameworks calculations

The calculations pertaining to intermolecular interactions were performed using the software suite Crystal-Explorer17 based on Gaussian B3LYP-D2/6-31G (d,p) molecular wave functions calculated using CIF files.⁶

S8: Face-indexed images

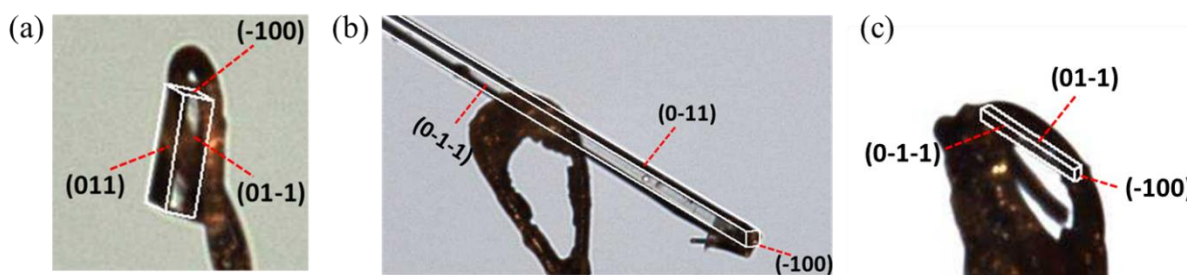


Fig. S1 Face-indexed images of crystals of (a) compound **4**, (b) compound **5**, and (c) compound **6**.

S9: Multiple elastic bending cycles and elastic twisting of crystal **4**

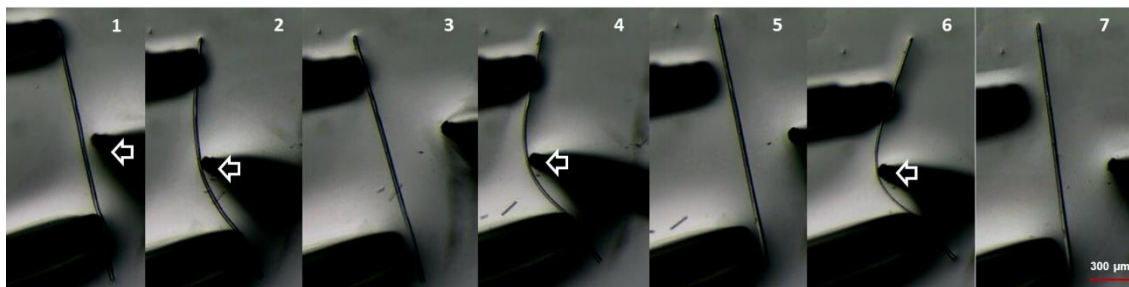


Fig. S2a Multiple elastic bending cycles of the crystal **4** from steps 1 to 7.

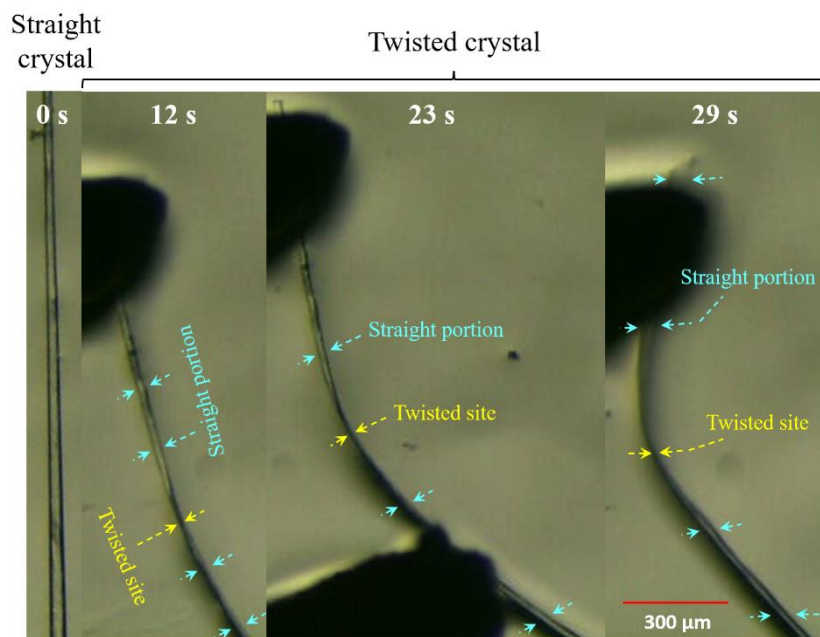


Fig. S2b Snapshots of elastic twisting of the crystal **4**.

S10: Maximum bending strain calculations

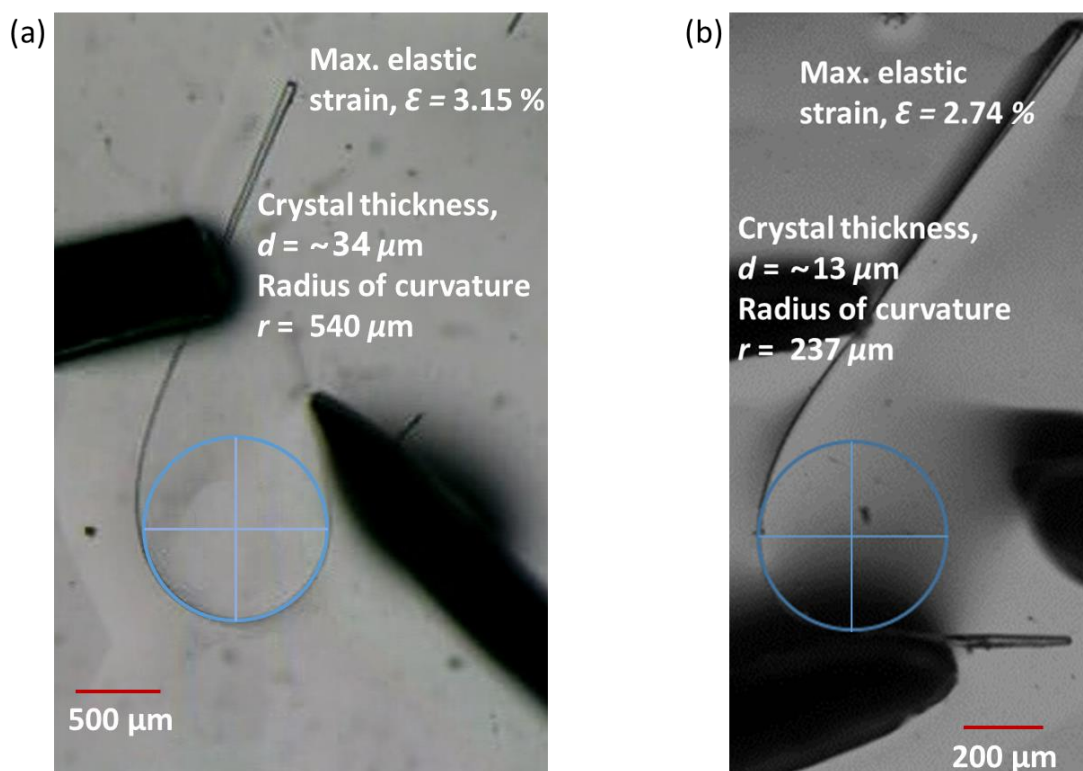


Fig. S3 Maximum bending strain calculations of two different crystals (a, b) of compound **4** prior to fracture.

S11: Load-displacement curves, and histogram plots of elastic modulus and hardness obtained from nanoindentation measurements

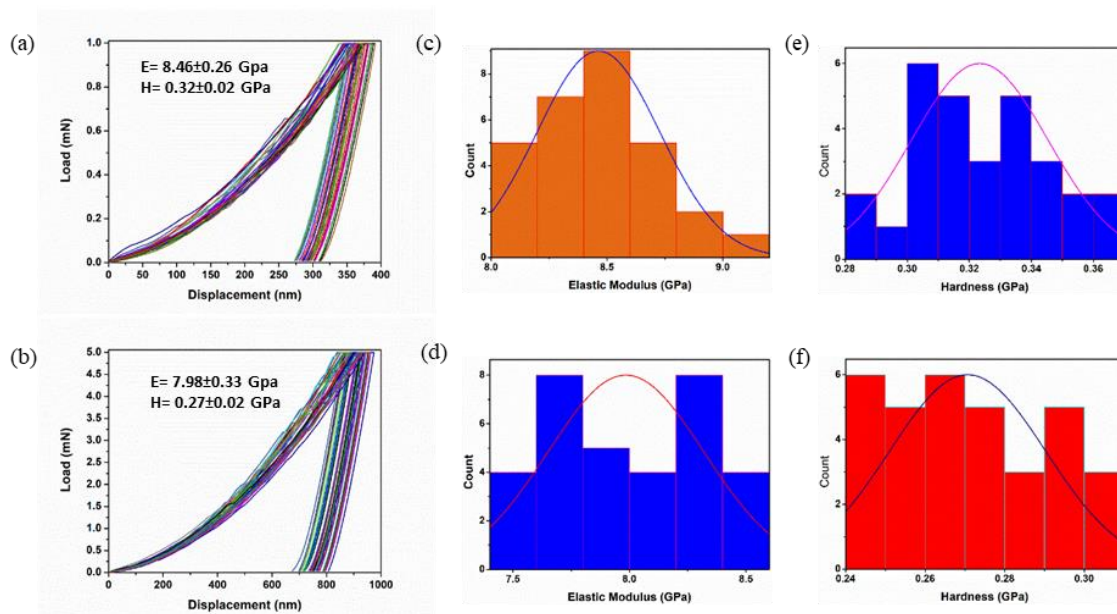


Fig. S4 Load-displacement curves (a) and (b), histogram plots of elastic modulus (c) and (d), and hardness (e) and (f), for 1 mN and 5 mN load, respectively, obtained from crystal 4.

S12: PXRD comparisons of simulated and experimental data

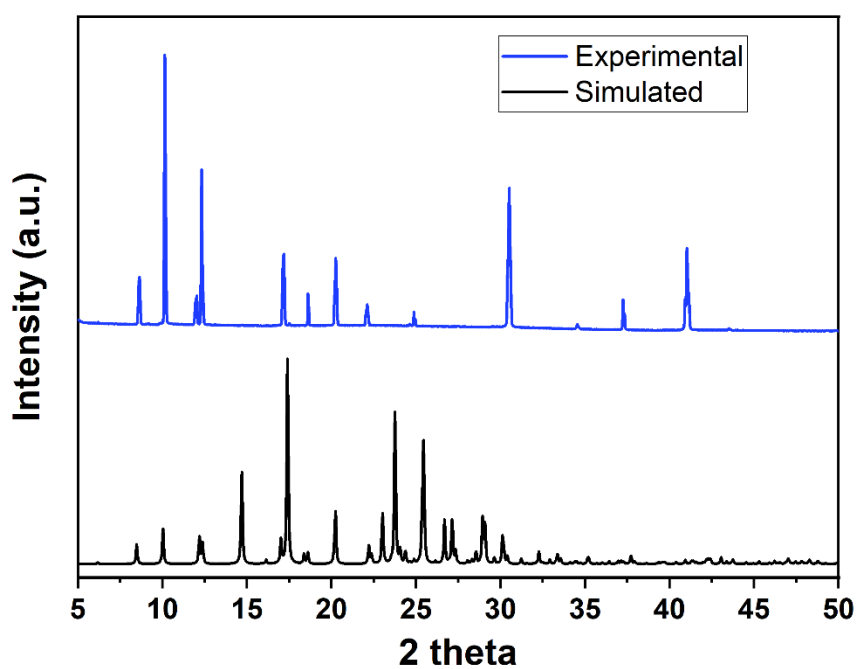


Fig. S5 Comparison of PXRD pattern of simulated and experimental data of crystal 4.

S13: DSC plot

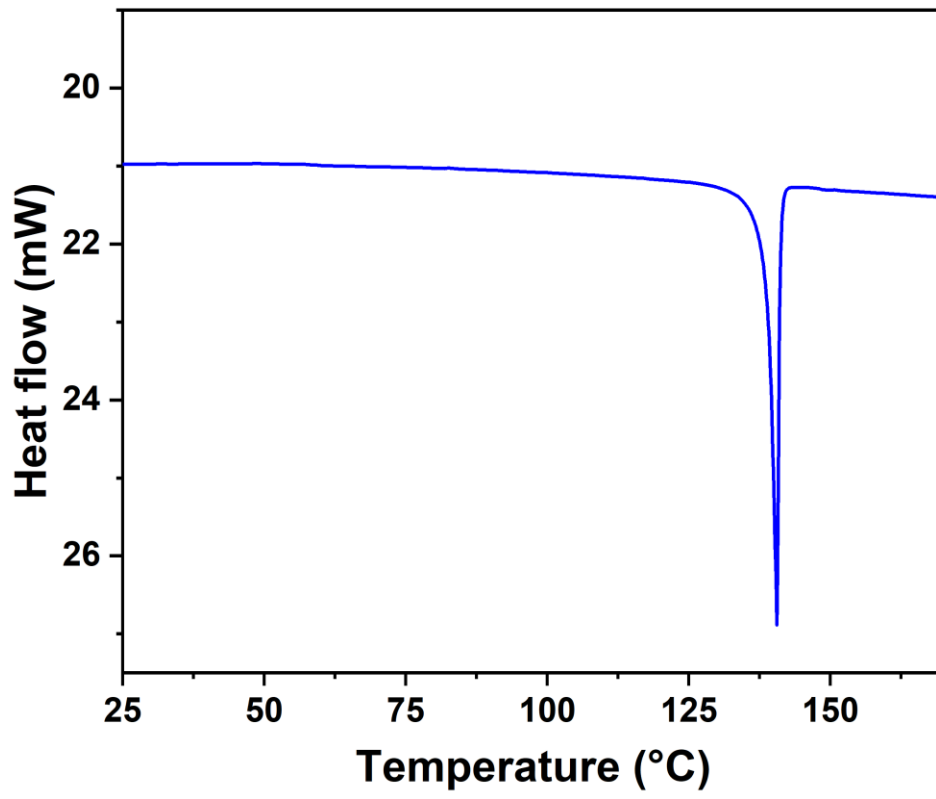


Fig. S6 DSC data of crystal 4.

S14: Crystal packing of compound 5 and 6

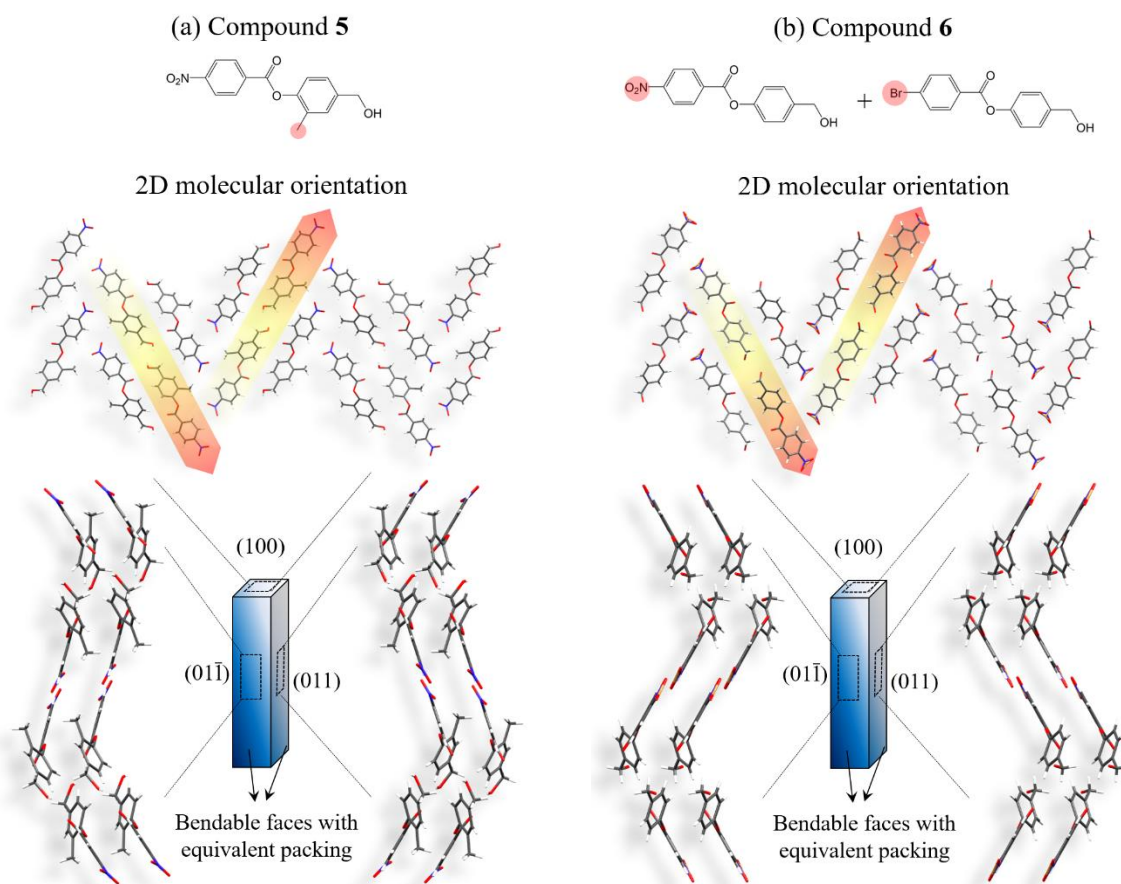


Fig S7: Crystal packing of 5 and 6 show equivalent arrangement for (011)/(0 $\bar{1}\bar{1}$) and (01 $\bar{1}$)/(0 $\bar{1}1$) faces as seen for 4.

S15: Mechanical bending experiments on crystals of compound 5, 6 and 7

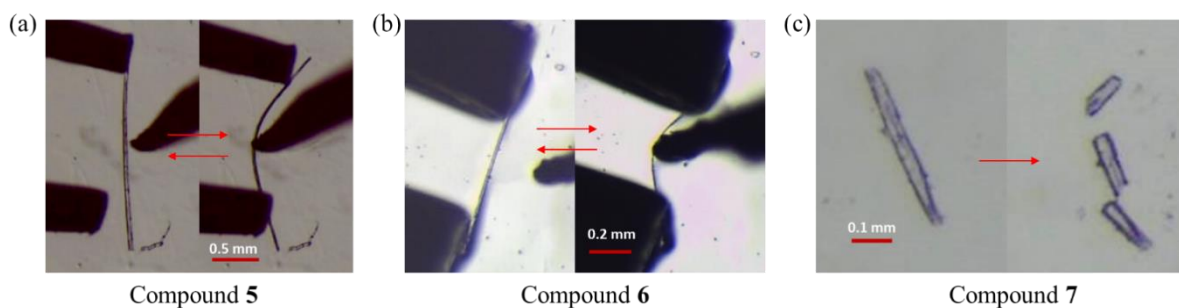


Fig S8: Reversible elastic bending of compound (a) 5, (b) 6, and brittle nature of (c) 7 under mechanical deformations.

S16: Histogram plots of elastic modulus and hardness for crystals of compound 5, 6 and 7

7

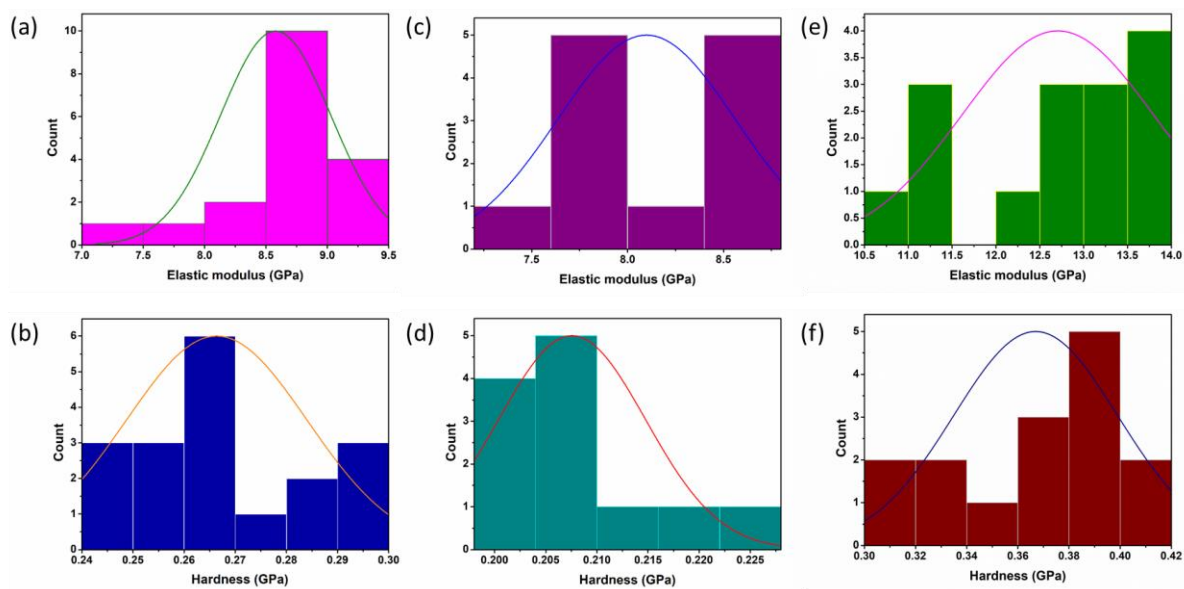


Fig. S9 Histogram plots of (a,c,e) elastic modulus (E) and (b,d,f) hardness (H). (a,b) Compound **5**: $E = 8.58 \pm 0.45$ GPa, $H = 0.27 \pm 0.02$ GPa. (c,d) Compound **6**: $E = 8.10 \pm 0.46$ GPa, $H = 0.21 \pm 0.01$ GPa. (e,f) Compound **7**: $E = 12.70 \pm 1.09$ GPa, $H = 0.37 \pm 0.03$ GPa.

S17: Crystallographic information table

Compound	4	5	6	7
Temp. (K)	293(2)	285(12)	293(2)	100.01(12)
Formula	C ₁₄ H ₁₁ NO ₅	C ₁₅ H ₁₃ NO ₅	C ₁₄ H ₁₀ Br _{0.10} N _{0.90} O _{4.80}	C ₁₅ H ₁₃ NO ₅
Molecular weight	273.247	287.274	275.62	287.26
Radiation	CuK α	CuK α	CuK α	CuK α
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1
<i>a</i> (Å)	4.00906(4)	3.9536(10)	4.0056(2)	6.97940(10)
<i>b</i> (Å)	11.18764(10)	11.2450(10)	11.2133(4)	7.62590(10)
<i>c</i> (Å)	28.5930(2)	30.6382(5)	28.6053(11)	12.34710(10)
α (°)	90	90	90	93.1440(10)
β (°)	90	90	90	97.3620(10)
γ (°)	90	90	90	94.0610(10)
<i>V</i> (Å ³)	1282.45(2)	1362.12(4)	1284.84(9)	648.752(14)
<i>Z</i>	4	4	4	2
ρ calc (g/cm ³)	1.415	1.401	1.425	1.471
μ (mm ⁻¹)	0.923	0.896	1.264	0.940
<i>F</i> (000)	570.255	600	569	300
θ range/°	3.09-68.25	2.885-68.02	3.090-68.100	3.617- 68.180
Reflections collected	12951	13435	10778	11974
Unique reflections	2328	2404	2128	4101
reflections <i>I</i> > 2 σ (<i>I</i>)	2192	2200	1760	4081
<i>R</i> 1	0.0387	0.0416	0.0484	0.0345
<i>wR</i> 2	0.1035	0.1231	0.1362	0.0927
<i>R</i> _{int}	0.0244	0.0407	0.0435	0.0421
Goodness-of fit	1.1213	1.073	1.064	0.990
CCDC No.	2269655	2311705	2311706	2311707

S18: Comparison of crystallographic parameters between 3 and 4

Compound	Space group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å ³)
3	<i>P2₁2₁2₁</i>	4	3.75	12.14	26.33	90	90	90	1198
4	<i>P2₁2₁2₁</i>	4	4.01	11.19	28.59	90	90	90	1283

S19: Supplementary Movies

Supplementary Movie S1 captured using Photron high-speed camera, and Supplementary Movies S2, S3, S4 and S5 captured using Leica camera.

References

1. L. Weinschenk, T. Gollnest, D. Schols, J. Balzarini and C. Meier, *ChemMedChem*, 2015, **10**, 891–900.
2. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
4. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst. A*, 2015, **A71**, 59-71.
5. W. C. Oliver and G. M. Pharr, *J. Mater. Res.*, 2004, **19**, 3–20.
6. M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, *CrystalExplorer17*, 2017. University of Western Australia. <http://hirshfeldsurface.net>.